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Morphology and Thermal Behavior of MCPA6/SAN Blends Prepared by Anionic Ring-Opening Polymerization of ε-caprolactam

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Summary

In this article, a series of blends of monomer casting polyamide 6 and styrene-co-acrylonitrile (MCPA6/SAN) were prepared by in situ anionic ring-opening polymerization of ε-caprolactam (CL). Their morphology and thermal behaviors were investigated by means of scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and wide-angle x-ray diffraction (WAXD), respectively. The SAN phase had much finer domain in MCPA6/SAN than that in the polyamide6/SAN (PA6/SAN) blends prepared by melt blending of PA6 and SAN. All the melting and crystallization parameters of MCPA6/SAN blends decreased gradually with the increase of SAN content, while the melting temperature was almost unchanged. These results were due to the hydrolysis reaction of SAN occurred during the anionic polymerization of ε-caprolactam (CL). In addition, WAXD results showed that only α crystal forms existed in the MCPA6/SAN blends.

Introduction

In the recent decades, a great number of literatures existed related to modification of polyamide 6. The blend components covered various polymers, among which styrenic copolymer, such as SAN, acrylonitrile-butadiene-styrene (ABS), hydrogenated styrene-butadiene-styrene (SEBS) have been widely investigated due to the significant commercial interest, especially ABS and SAN [1-13].

Due to thermodynamical immiscibility, the polyamide-containing binary blends usually exhibited poor phase dispersion and interfacial adhesion, which in turn resulted in unsatisfactory mechanical properties. Therefore, there were extensive interests in improving their compatibility. One of preferable routes was reactive compatibilization, in which graft or block copolymers were formed in situ during melt processing in terms of appropriate reactive functionalities. It had emerged as an effective way of solving the problem associated with incompatible polymer mixtures [14].

Jafari et al. studied that the effects of added SANMA on the thermal behavior and morphology of multicomponent blends based on PA6, PA6/SAN and PA6/ABS [15,16]. Paul and coworkers used imidized acrylic polymers (IA) or styrene-acrylonitrile-maleic anhydride (SANMA) terpolymer as a compatibilizer for PA6/ABS and PA6/SAN blends, respectively, and studied the phase morphology and phase inversion behavior cover the complete range of compositions [4-10]. Liu et al.[11] converted the nitrile groups of the SAN into oxazoline groups by condensation reaction with aminoethanol, both in a Brabender batch mixer and in a twin-screw extruder, and the morphological studies indicated that such modified SAN copolymers could be used as compatibilizers for PA/SAN blends and PA/ABS blends. Ohishi et al.[12] investigated the phase morphology and the compatibilization mechanism of PA-6/ABS blends compatibilized with SAN and polyarylate (PAr) block copolymer (SAN–PAr) and showed how effective the SAN–PAr block copolymer was on their impact energy absorption control. Cho et al. [13] reported the effects of reactive reinforced interface on the morphology and tensile properties of amorphous polyamide (α-PA) and SAN blend have been investigated using SANMA copolymer as a reactive compatibilizer. In addition, in situ polymerization was another effective way to control morphologies of polymer blends in order to improve the dispersion. In this method, much attention had mainly focused on rubber- or thermoplastic-modified thermoset polymer, e.g. epoxy resins/thermoplastics systems [17-20]. It had been shown that the blend morphologies could be controlled by both dissolution/diffusion of thermoplastics in the polymerizable monomer and thermodynamics combined with reaction kinetics [21].

In our laboratory, a novel approach for improving toughness of PA 6 had been explored [22]. The approach was that another polyamide, i.e. polyamide 66 (PA66), was used to toughen MCPA6. By in situ anionic polymerization of CL with PA66 dissolved in it, and a small content of PA66 could dramatically improve toughness of MCPA6/PA66 blends. According to this way, we attempted to add the SAN content to MCPA6. The purpose of this study was to explore the phase morphology and the thermal behaviors of MCPA6/SAN blends prepared by in situ anionic ring-opening polymerization. The two-phase nature of ABS materials plus their high melt viscosity/elasticity complicated the morphological and the thermal behavioral study of MCPA6/ABS blends [7]. Thus, the MCPA6/SAN blends were useful for the better understanding of the morphology development and thermal behaviors. It was of particular interest to show that the reactive compatibility between MCPA6 and SAN by the possible side-reaction of SAN content occurred under alkaline condition in the anionic ring-opening polymerization of CL. Both the reactive compatibility and the polymerization process were carried out simultaneously. In addition, polyamide 6 was directly melt-blended with SAN copolymer according to the same composition as MCPA6/SAN, which was designated as PA6/SAN.

Experimental

Materials

Styrene–acrylonitrile copolymer (SAN, AS-127H) was supplied by Chimei Corporation (Taiwan, China), and it contains 34wt% acrylonitrile. PA6 (YH-600) was provided by Baling Shihua Chemical and Synthetic Fiber Co., Ltd (Yueyang, Hunan,

China). Prior to each processing step, all polyamide-containing materials were dried in a vacuum oven for at least 24h at 80°C to remove absorbed water. CL was obtained from Joint Stock Company, Republic of Belarus. Sodium hydroxide (NaOH) and toluene diisocyanate (TDI) (analysis purity) used in this work were purchased from Shanghai Chemical Reagents Company without further treatment.

Preparation of MCPA6/SAN and PA6/SAN Blends

SAN was firstly dissolved in CL monomer at 170°C under nitrogen until a homogeneous transparent solution was obtained. The resulting mixture was vacuumed at 170°C for 20min to remove water, followed by addition of 1.2wt% sodium hydroxide (NaOH) under stirring. Afterwards, vacuum was kept for another 20min and then 1.2wt% toluene-2, 4-diisocyanate (TDI) was added. Immediately, the mixture was poured into a mold preheated at 180°C, polymerized in the oven at 180°C for 30 min, and subsequently cooled at 35°C. After extracted for 5h with boiling water to eliminate the residual monomer, and the MCPA6/SAN blends were dried in a vacuum oven for 24h at 80°C, then directly carve into standard testing specimens according to ASTM.

For comparison, another series of PA6/SAN blends were prepared by melt extrusion in a corotating twin-screw extruder (Φ=35mm, SHJ-30) at 240rpm. The barrel temperatures are 230~250°C. The pellets were dried in a vacuum oven for 24h at 80°C and then injection-molded into standard Izod impact specimens in an injection-molding machine (SZ-160/80 NB) at 230°C.

Characterization

The cryo-fractured surface of samples in liquid nitrogen were etched in tetrahydrofuran (THF) for 24h at ambient temperature to remove SAN domains, followed by sputtered with gold prior to scanning electron microscope (SEM, JSM-6360LV, JEOL) examinations.

After extracted in THF for 72h, SANs in the MCPA6/SAN blends were recovered directly by the evaporation of the solvent. In order to further confirm the side reaction occurred in MCPA6/SAN system, the dried SAN was firstly solved in CL at 170°C, after the CL monomer was vacuumed at that temperature for 30 min, the resulting mixture was dissociated at 180°C for 300 min in order to the dissociation reaction of SAN was fulfilled to a great extent. The resulting solution was a transparent liquid. Water was used to scour off the residual CL monomers at room temperature, and then the precipitate was dried in vacuum oven at 100°C. And all of the above samples were measured by Fourier transform infrared spectroscopy in its attenuated total reflectance mode (ATR-FTIR). ATR-FTIR was recorded with a Nicolet AVATAR 360 apparatus. The scan times were 32 scans with a resolution of $4cm^{-1}$.

Differential scanning calorimeter (DSC) measurements were carried out on a NETZSCH DSC 200 PC under nitrogen atmosphere at a heating/cooling rate of 10°C/min. The samples were firstly heated to 250°C and maintained for 2 min to erase any previous thermal history. The crystallization and melting thermograms were taken from the subsequent cooling and the second heating cycles.

The Wide-angle X-ray diffraction (WAXD) was performed on a X-ray diffraction analyzer (XRD, Rigaku D/Max-III Japan) equipped with a rotating Cu anode

generator system using Cu/K-alpha1 (λ=1.540Å) radiation. The diffraction angles (2θ) were from 5° to 50°. The data were accumulated for 6s at angular intervals of 2θ=0.1°.

Results and Discussion

SEM analysis

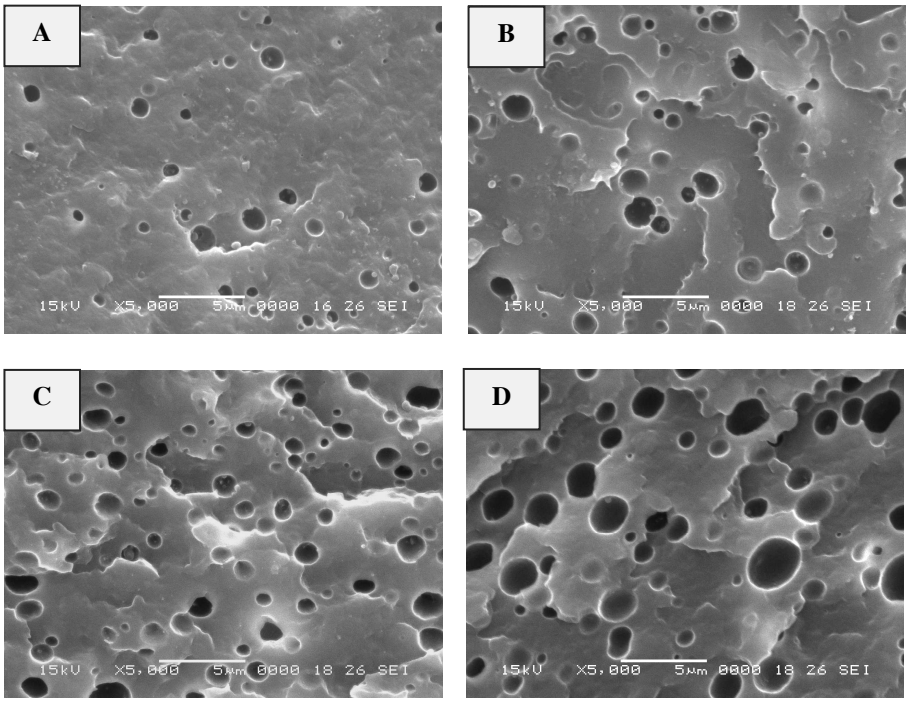


Figure 1. SEM micrograph of the fractured surface of the PA6/SAN blends containing different SAN content (at magnifications of ×5000) (A): 2.5% SAN; (B): 5% SAN; (C): 10% SAN; (D): 15% SAN

In order to make the dispersed domain clearly visible, the SAN content was selectively etched with tetrahydrofuran (THF). Figure 1 (A)-(D) showed the etched SEM micrographs of PA6/SAN blends with different SAN content, respectively. As expected, the PA6/SAN blend exhibited a distinctly two-phase structure because of their poor compatibility. The domain size increased from 1~1.5 μm to 3 μm in diameter with addition of SAN content up to 15%. This might be attributed to coalescence of SAN domains at higher concentration.

However, compared to PA6/SAN blends, a marked difference in the morphology could be observed for MCPA6/SAN blends. At a low SAN content (Figure 2A), the domain size of SAN was too small to be almost observed at the present magnification. Although the size of dispersed phase increased with addition of SAN, similar to the PA6/SAN blends, the diameter of dispersed particles was about 200nm even at SAN

content of 15%; the size distribution was more uniform. The above observation suggested that a finer dispersion of the SAN phase in the matrix be achieved in terms of *in situ* anionic ring-opening polymerization of CL.

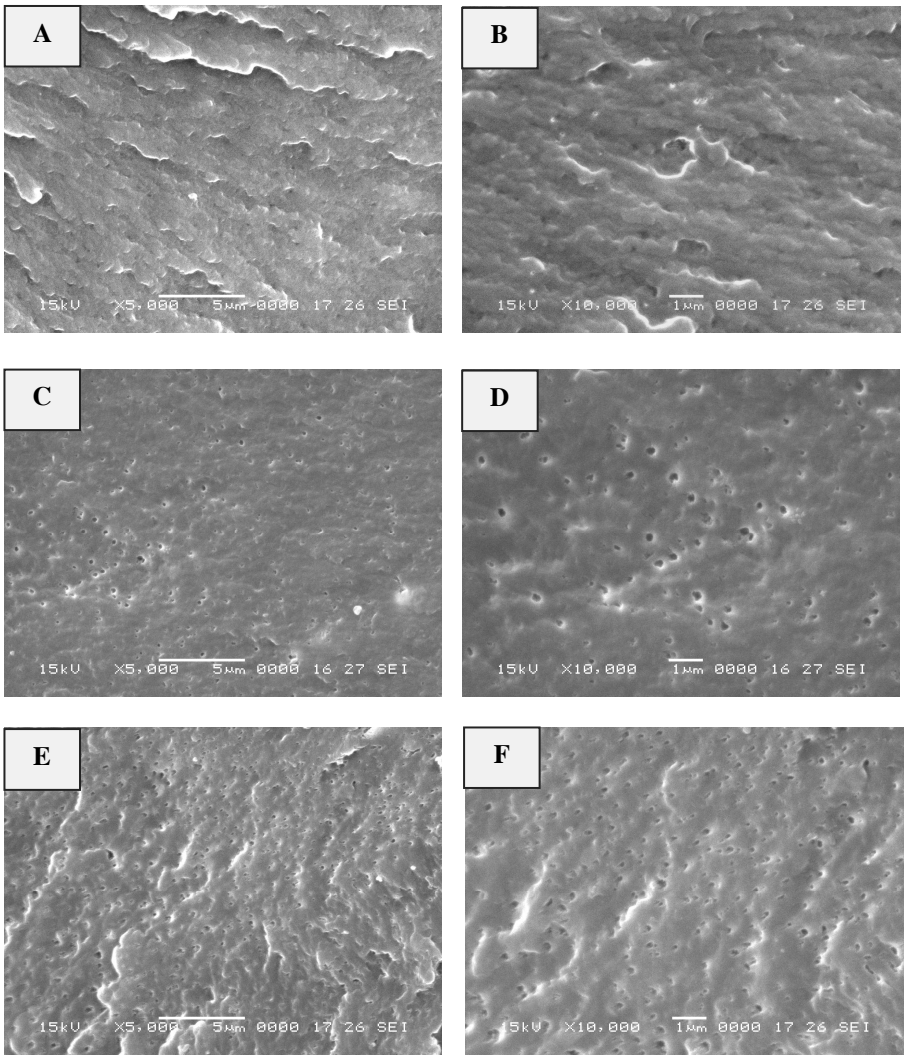


Figure 2. SEM micrograph of the fractured surface of the MCPA6/SAN blends containing different SAN content (at magnifications of ×5000 and×10000). A, B: 2.5% SAN; C, D: 10% SAN; E, F: 15% SAN

According to our knowledge, the improved dispersion might be attributed to the following two factors in the MCPA6/SAN system. Firstly, it was expected that phase separation would be impeded effectively, because of high rate of anionic ring-opening polymerization that usually fulfilled within a few minutes. Secondly, the hydrolysis reaction occurred for CN groups of SAN under sodium hydroxide solution. The resulting products might improve the compatibility between MCPA6 and SAN.

FTIR analysis

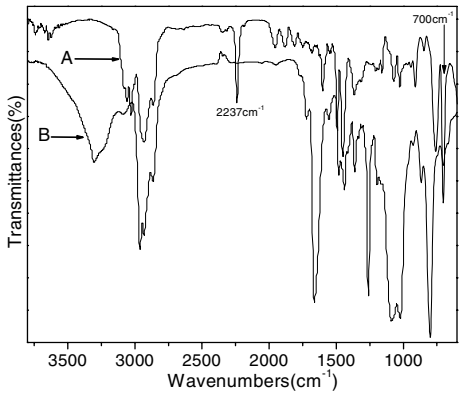


Figure 3. FTIR spectra of SAN in different blends A: PA6/SAN; B: MCPA6/SAN

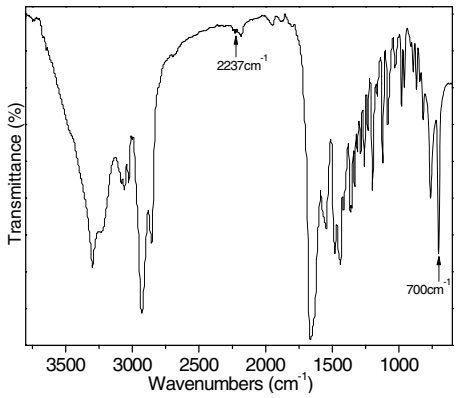
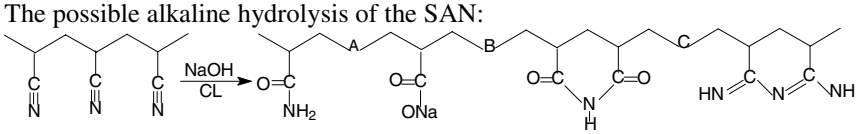


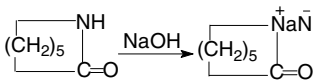
Figure 4. FTIR spectra of the products after hydrolysis in ε-caprolactam

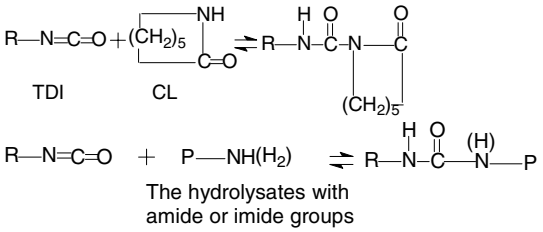
To confirm the above hydrolysis reaction, the SAN component in the above blends was firstly extracted by THF. After evaporating the THF solvent, the product was analyzed by means of ATR-FTIR. Figure 3 showed the infrared spectra of both PA6/SAN and MCPA6/SAN blends, respectively. In the PA6/SAN blend, the vibration peak of CN group at 2237cm^{-1} could be clearly observed, whereas for the MCPA6/SAN blend, no peak was observed at the corresponding wavenumber. However, the two additional peaks at 3300cm^{-1} and 1650cm^{-1} occurred, which corresponded to the amide group [23]. That was to say, the hydrolytic reaction of SAN did occur under alkaline condition, and the resulting groups, similar to those of the MCPA6 matrix, might improve the compatibility of MCPA6/SAN blends and the dispersion of SAN. Figure 4 was the IR spectra of the dried precipitate, which were the products of SAN subjecting side reaction in CL solvent at high temperature. There is no obvious peak in about 2237cm^{-1} but a peak in about 700cm^{-1}, which is the absorption of benzyl ring in SAN; The peaks at 1650cm^{-1}and 1550cm^{-1}was the characteristic absorbency of the carbonyl group existing in CL, it was to say that the SAN hydrolysis did occur in CL solution at a high temperature. The SAN hydrolysis resulted in similar structures, such as amide, imide, and so on.[24-26] All these groups had a good compatibility with the MCPA6 matrix. In addition, besides CL formed activator with TDI (the initiator) to initiate the polymerization of CL, the amide could react with TDI rapidly; the resulting molecules could act as macromolecular activator and initiate the polymerization of CL to form block copolymer. The wholly chemical schemes of the reaction process could be summarized as follows:

The possible alkaline hydrolysis of the SAN:

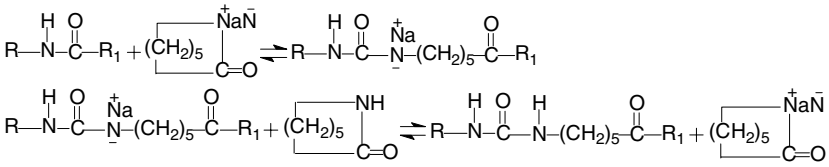


Activation:

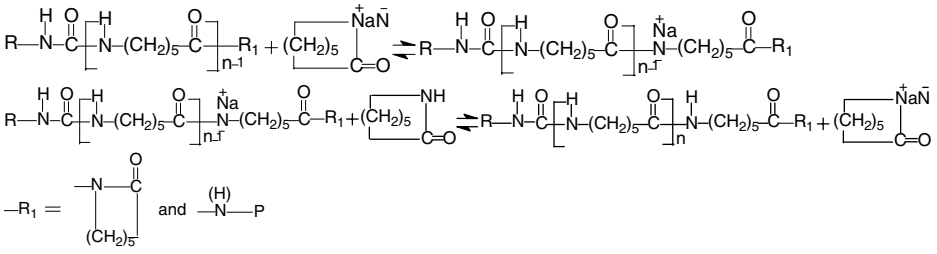




Initiation:



Propagation:



DSC analysis

Table 1. Melting and crystallization parameters for MCPA6/SAN blends

	Heating (2nd)			Cooling		
MCPA6/SAN (w/w)	T_m (°C)	ΔH_m (J/gPA6)	X_{DSC} (%)	ΔH_c (J/gPA6)	T_c (°C)	ΔT_c (K)
100/0	214.3	-55.86	29.00	64.73	169.4	44.9
100/2.5	213.7	-50.76	26.72	55.68	165.9	47.8
100/5.0	212.8	-47.70	25.11	51.70	163.0	49.8
100/10	213.0	-46.30	-24.53	57.11	161.3	51.9
100/15	212.3	-45.58	23.99	48.92	159.2	53.1

Figures 5 (A, B) showed the cooling and the second heating DSC scans of various MCPA6 blends. The melting and crystallization parameters for pure MCPA6 and MCPA6/SAN blends were summarized in Table 1. As indicated from Figure 6 and Table 1, the ΔH_m, ΔH_c and T_c decreased gradually in MCPA6/SAN blends, but the degree of super cooling ($\Delta T_c = T_m - T_c$) values showed the opposite trend. Additionally, the melting temperature (T_m) of MCPA6 portion for the MCPA6/SAN blends was almost independent of blend. Such above-mentioned results indicated that the SAN and/or the hydrolyzed SAN tended to interfere with the crystallization of the MCPA6 in various blends because of its fine dispersion and the hydrolysis of the SAN. But the

SAN content had little effect on the crystalline structure. However, Jafari [15] found that all the PA6/SAN melt blends showed a significant increase in nucleation ability, crystalline degree and crystallization rate of PA6 due to the addition of SAN, and SAN played a more major role in controlling the crystallization behavior of PA6.

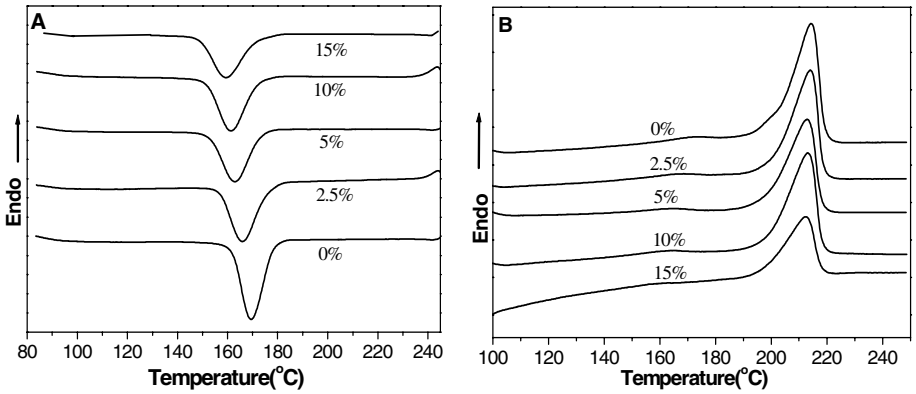


Figure 5. Thermograms of MCPA/SAN blends with different SAN contents (A): cooling; (B): heating

WAXD Analysis

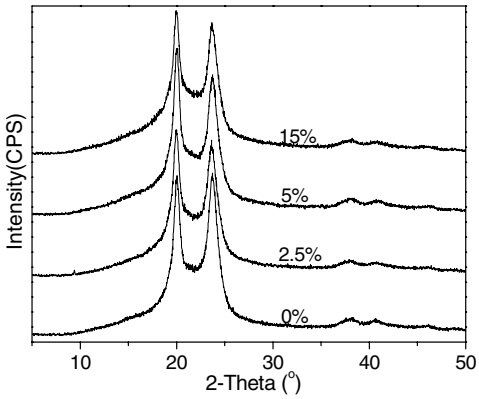


Figure 6. Wide-angle X-ray diffraction spectra of MCPA6/SAN blends with different SAN contents

WAXD spectra of MCPA6 and its blends with SAN were showed in Figure 6. It could be seen that all the MCPA6/SAN samples exhibited only α crystal form, which corresponded to the crystallographic planes (200) and (002+202) [27-29]. The α structure was known to be more thermally stable and can be obtained by slow cooling of the melt [30]. Once the α form crystal formed, it was difficult to change over from α to γ form crystal. Otherwise, the α crystal form did not show any significant change with the different SAN content in our study. There had hardly any change of the α form crystal with the improved compatibility of the two polymers.

Conclusions

In this study, MCPA6/SAN blends were prepared by *in situ* anionic ring opening polymerization technique. SEM micrographs of the blends showed that SAN had a finer dispersion in the MCPA6/SAN blends than that in the PA6/SAN blends prepared by direct melt blending of PA6 and SAN. This could be attributed to rapid anionic polymerization and hydrolysis of CN groups of SAN. This hydrolysis product increased the compatibility between SAN and MCPA6. FTIR results confirmed the hydrolysis reaction. The results of the DSC cooling process showed that the ΔH_m, ΔH_c and T_c decreased gradually in the MCPA6/SAN blends. The crystallization of MCPA6 was inhibited by the presence of SAN. But the T_m of MCPA6 portion for the MCPA6/SAN blends was almost independent of blend. Only α crystal form of the MCPA6 existed in the blends by means of WAXD.

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